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(54) Title: PROCESS FOR TREATING AN AQUEOUS KF WASTE STREAM AND FOR CONVERTING KF INTO HF AND KOH			
(57) Abstract			
<p>The present invention is directed to a process for treating an aqueous KF waste stream comprising at least one treatment step selected from the group consisting of inert gas stripping the aqueous KF waste stream, passing said waste stream through a carbon bed, concentrating said waste stream or a combination thereof to remove dissolved organic compounds. The present invention is also directed to subjecting the treated KF waste stream to electrodialytic splitting in a water splitting cell to form HF and either KOH or an acid depleted salt stream. The dilute HF can be concentrated to a concentrated and commercially viable product.</p>			

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**PROCESS FOR TREATING AN AQUEOUS KF WASTE  
STREAM AND FOR CONVERTING KF INTO HF AND KOH**

This invention relates to a process of treating an aqueous KF waste stream and converting KF (potassium fluoride) into HF (hydrogen fluoride) and KOH (potassium hydroxide). More particularly, the invention is directed to a process for removing dissolved organic compounds from an aqueous KF waste stream by at least one treatment step selected from the group consisting of inert gas stripping the aqueous KF waste stream, passing said waste stream through a carbon bed, concentrating said waste stream or a combination thereof. The stripped waste stream is then subjected to electrodialytic splitting to convert KF and water into HF and KOH.

**Background of the Invention**

Many industries use HF in processing. For instance, the alkylation industry uses HF as a solvent/catalyst in the process of producing gasoline. This process generates waste HF stream, which when scrubbed with KOH produces a second waste stream containing KF. Other industries producing KF waste include glass etching processing, nuclear industry (UF<sub>6</sub>), stainless steel pickling and specialty metals processing.

In industrial waste processes, HF gas and liquid streams are neutralized with water, NaOH, KOH or lime to form an aqueous solution containing organic compounds and KF or NaF or insoluble CaF<sub>2</sub>. Most of the organic phase is recycled. When KOH is used as the scrubbing medium, the KF is generally reacted with lime or Ca(OH)<sub>2</sub> to form KOH and to precipitate the fluoride as CaF<sub>2</sub>. The KOH can be recycled, for example, for scrubbing more HF streams which recovers the potassium value; however, the insoluble CaF<sub>2</sub> is disposed of as a waste which loses the fluoride value. The insoluble CaF<sub>2</sub> solid or slurry must be landfilled or deep well injected. Disposal sites for CaF<sub>2</sub> are scarce and costly, and are subject to increasing environmental regulations. It is therefore desirable to avoid making CaF<sub>2</sub>, which is difficult to dispose of, and instead recover and recycle the fluoride value along with the potassium value of the KF.

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USP 3,787,304 discloses a process for regenerating KF from fluorosilicic acid via neutralization with KOH electrolytic water splitting to produce HF and KOH.

However, aqueous KF waste is not directly suitable for electrolytic water splitting. The harmful and undesirable impurities in the KF waste will foul the membranes, interfere with cell operation, and contaminate the HF and KOH products. Furthermore, the dilute HF (~10%) product obtained from the water splitting cell is not commonly used or commercially viable.

There is a need for an effective process to treat aqueous KF waste streams to recover both potassium and fluoride values. Since electrolytic water splitting will convert KF into HF and KOH both the potassium and fluoride values can be recovered. However, there is a need to treat a waste KF stream to make it suitable for electrolytic water splitting treatment. Further, there is a need to convert the nonuseful dilute HF product obtained from electrolytic water splitting into a more concentrated and commercially viable product.

#### Brief Description of the Drawings

Fig. 1 illustrates a steam stripping schematic.

Fig. 2 illustrates a three compartment water splitting cell.

Fig. 3 illustrates a schematic flow chart used to practice the present invention.

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#### Detailed Description of the Invention

The present invention is directed to a process of treating an aqueous KF waste stream to reduce dissolved undesirable organic compounds comprising at least one treatment step selected from the group consisting of inert gas stripping the aqueous KF waste stream, passing said waste stream through a carbon bed, concentrating said waste stream or a combination thereof. The present invention is also directed to splitting the KF in the treated KF waste stream by introducing the treated KF waste stream into an electrolytic water splitting apparatus which produces HF and KOH. The HF stream may be distilled to provide a purer and more concentrated HF, which in turn can be converted to anhydrous HF.

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As shown in Fig. 1, the KF waste stream (10) is introduced into the top of the stripping column (14) and gas (12) is introduced at the bottom. The stripping gas must be inert to the KF and organics and is preferably selected from steam, air, methane, nitrogen, helium or a combustion gas such as from an indirect fired boiler or other sources of clean flue gas. Preferably, at least 50 to 85% of the dissolved organics are removed when gas stripping is utilized. After stripping, an effluent stream containing organics (16) is removed from the top of the stripping column, and then further treated and/or discharged. The steam stripped KF waste stream (18) exits from the bottom of the stripping column.

Alternatively the undesirable dissolved organics may be removed by concentrating the KF waste stream by known methods such as evaporation or distillation. As the concentration of KF in the KF waste stream approaches 50 weight %, the amount of undesirable organics which is separated approaches 90%. Thus, the KF in the KF waste stream is preferably concentrated to at least about 20 weight %, more preferably to at least about 30 weight % and most preferably to between about 30 weight % and about 50 weight %. Any volatile organics are removed with the water which is being evaporated. Any organic layer which is formed may be conveniently separated by known techniques.

Preferably, the stripped KF waste stream is more concentrated than the aqueous KF waste feed stream. For instance, about 30 to about 50 weight % KF strength may be obtained from about 15 to about 20 weight % KF feed. The concentration of the feed stream is preferably between about 15 and about 20 weight %. Since concentrated KF is more economical to transport than dilute KF, the KF may be stripped at the source of waste generation and then shipped to a central location for further processing.

The gas stripper may be run at any pressure. However, for reasons of convenience and economy, atmospheric pressure is generally used. the gas may be introduced at any pressure. The higher the gas stripping temperature, the greater the organics removal. For this reason, temperatures between about 100° to about 125°C are preferred. The organics removal also increases as the gas/feed ratio increases. The stripping temperature may be

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conveniently maintained by heating the stripping gas and/or the KF feed solution.

The present invention is also directed to subjecting the treated KF waste stream to electrodialytic water splitting. The treated KF waste stream is introduced into an electrodialytic water splitting apparatus having at least one water splitting cell under the influence of direct current. Two or more cells may be stacked to form a cell stack. For large scale regeneration processes up to about 200 cells are included in each stack.

The water splitting cell is preferably a three compartment bipolar, anion and cation membrane cell. In a three compartment cell, the water and KF are split and the resulting ions are recombined to form HF and KOH. Three-compartment electrodialytic water splitting cells are well known in the art and are described in, for example, U.S. Patents 4,740,281 and 5,135,626 which disclosures are hereby incorporated by reference in their entirety.

An alternative water splitting cell is a two compartment cation bipolar cell which converts water and KF into KOH and an acidified salt stream. If both KOH and HF are desired, an additional step converting the acidified KF would be required. Two-compartment cells are described in, for example, USP 4,390,402 which disclosure is hereby incorporated by reference in its entirety.

A three compartment water splitting cell is shown in Fig. 2. Bipolar (22), anion (24) and cation (20) permeable membranes are arranged to form acid (A), salt (S) and base (B) compartments. Direct current is passed through the cell using an anode (26) and a cathode (28).

The aqueous KF waste stream (30) is introduced into the salt compartment and water (32) is introduced into the base and acid compartments. Under the influence of the direct current, the KF is split into  $K^+$  and  $F^-$  ions. The  $K^+$  is transported across the cation membrane into the base compartment. The  $F^-$  is transported across the anion membrane to the acid compartment. The bipolar membrane splits water to provide  $OH^-$  ions for the base compartment to form KOH and  $H^+$  ions to the acid compartment to form HF. A KOH stream (34) is obtained from the base compartment, a HF

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stream (36) is obtained from the acid compartment and a depleted salt solution (38) is obtained from the salt compartment.

Electrodialytic water splitters can be obtained from AlliedSignal Inc.'s Aquatech Systems unit, Asahi Glass and Graver Inc. Preferred cation membranes are CMV cation membranes from Asahi Glass, perfluorinated cation membranes such as NAFION by DuPont, and the membranes disclosed in USP 4,738,764 which are commercially available from AlliedSignal Inc. Preferred bipolar membranes have low diffusivity for KF and HF, such as those disclosed in USP 4,116,889 and commercially available from AlliedSignal Inc.'s Aquatech Systems unit. Preferred anion membranes are polystyrene-vinylbenzylchloride polymer membranes available from AlliedSignal Inc. through Aquatech Systems and AMV or AMP membranes available from Asahi Glass.

The concentration of the treated KF waste stream introduced into the water splitting cell is from about 1 to about 50 wt %, preferably from about 15 to about 20 wt %. Weaker solutions can be concentrated, and stronger solutions can be diluted to the preferred range whereas the preferred range does not require concentration or dilution of the KF solution.

Depending on the cell efficiency, different concentrations of HF and KOH are obtained. Generally, a three-compartment water cell converts greater than about 70 % KF to HF, and a two-compartment cell converts greater than about 50 %. Preferably, at least 5 wt % HF stream and at least 15 wt % KOH stream is obtained. In operations of most three-compartment water cells, the resulting HF stream contains approximately 10 wt % HF and the resulting KOH stream contains approximately 18 wt % KOH. However, any concentrations of the HF and KOH obtained by electrodialytic splitting are within the scope of the present invention.

The process of the present invention is especially suited for alkylation KF waste. Types of KF waste from the alkylation industry include ARN-KF and ASO-KF and mixtures thereof. Acid Relief Neutralizer (ARN-KF) comes from a gaseous stream containing HF and volatile organics that is neutralized with KOH. ARN-KF contains low levels of organics, typically but not limited to less than 300 ppm Total Organic Carbon (TOC). Acid Soluble Oil (ASO-KF) comes from

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a liquid HF and an essentially non-volatile organic stream that is neutralized with KOH. ASO-KF contains higher levels of organics, typically but not limited to 1500 to 12,000 ppm TOC.

To maximize production and minimize cost, the water splitting membrane cell should operate continuously without frequent shutdowns or interruptions. The water splitting membrane cell operation depends on the quality of the ARN-KF and ASO-KF. The low levels of organics typically found in ARN-KF (generally <50 ppm as TOC) are not harmful to the membranes. Therefore ARN-KF may not require gas stripping. However, ASO and ARN-ASO combined streams must have most of the undesirable organics removed prior to electrodialytic water splitting. Undesirable organics foul the membranes causing the voltage across the cell to increase and the current to decrease thus decreasing efficiency and product quality. Solid materials will foul and embrittle the membranes. Cell production rates of HF and KOH, purity of the products, and membrane life will also suffer. If the membranes foul, they will fail and need to be replaced thus causing production stoppages, higher maintenance costs, and poor overall operation economics.

The aqueous KF waste stream introduced into the water splitting cell should be homogeneous and contain no floating or insoluble organics. Preferably, the KF is colorless and odorless. Thus, in addition to the gas stripping treatment step to remove the major portion of undesirable organic impurities described above, the present invention is directed to additional treatment steps used prior to the electrodialytic water splitting.

Insoluble organic or inorganic material may be removed from the aqueous KF waste stream by filtration, skimming, or decanting, or other suitable means. Preferably, the insoluble material is removed prior to the gas stripping step.

The gas stripped KF waste stream can be passed through a carbon bed to remove remaining organics. Gas stripping generally removes about 50 to about 85% of the undesirable organics although the actual percentage of organics removal depends on the species of organics present and their volatility characteristics and the gas stripping conditions. The carbon bed in effect polishes the waste stream to remove residual undesirable organics.



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In fact, all undesirable organics could be removed using only a carbon bed, but the cost of operation, such as carbon replacement, is very expensive. Using both gas stripping and a polishing carbon bed minimizes the cost of organics removal. The majority of the organics are removed by gas stripping and the remaining small amounts of organics are removed with a polishing carbon bed.

Different activated carbons can be used to remove the organics, such as most coal and coconut shell based carbons. Coconut type carbons are preferred due to their lower levels of silica and metal impurities. Silica and metal tend to leach into the KF if the pH of the KF stream is not properly adjusted.

Generally, pH and temperature do not greatly affect the adsorption efficiency of the carbon bed and therefore, organics removal. Particle size on the other hand affects the pressure drop of the carbon bed; therefore adsorption efficiency and particle size have to be balanced to meet operating conditions.

Often the waste streams, particularly ASO-KF contain acetates in varying amounts, which can not be removed by either gas stripping or carbon absorption. However, acetates do not foul the membranes of the water splitting cell so removal is not necessary for successful cell operation. Acetates and residual organics may be removed by known methods in the art if product quality is a concern.

After gas stripping, but before passing through a carbon bed, the pH of the stripped KF waste stream is preferably adjusted by adding HF or KOH. The pH of the waste stream is preferably adjusted to pH 6-8. It is difficult to adjust the pH of KF streams below pH 7 due to the intense buffering effect of  $\text{KHF}_2$  from pH 7 to pH 3. The flat nature of the pH curve below pH 7 indicates that a large addition of acid gives a small change in pH. Because of this, the pH adjustment is most preferably controlled to pH 7-8.

It is important to adjust the pH since an acidic stream may present corrosion and materials of construction problems and an alkaline stream may contain carbonates which adversely affect the membranes. Carbonates decompose under the acidic conditions inside the water splitting cell causing damage to the membranes because the  $\text{CO}_2$  gas bubbles restrict solution flow around membranes.

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Adjusting the pH also precipitates silica compounds in the feed and prevents leaching of silica from the carbon beds if a carbon separation is later used. Silica compounds may be leached by either alkaline or acidic KF streams and can precipitate in the cell stack  
5 where the pH and HF concentration change rapidly. The silica compounds precipitate as potassium hexafluorosilicate plugging filters, gaskets, and causing fouling and embrittlement of the membranes themselves leading to unacceptable pressure drops. Leaching of silica compounds is minimal from pH 6-8.

10 Adjusting the pH will also precipitate many undesirable heavy metals. Metal impurities such as calcium, magnesium, and heavy metals such as but not limited to iron, nickel, copper, and arsenic could lead to membrane fouling. The most objectionable are the heavy metals that can form insoluble salts on the membranes or are  
15 insoluble at various pH values. If these metals are present in significant quantity (> 50 ppm), they must be removed prior to electrodialytic water splitting to prevent fouling and/or embrittlement of the membranes.

ARN-KF and ASO-KF waste streams are generally low in metal  
20 content and do not require further treatment. However, further treatment may be required for waste streams containing heavy metals not removable by pH adjustment.

It is preferable that the KF not contain chloride impurity because it is difficult to remove and is undesirable in the 38% HF  
25 product. It is also preferable that the KF waste stream not contain other non-volatile impurities such as sulfates and phosphates. The KF streams must pass the Priority Pollutant and TCLP tests such that the waste can be considered non-hazardous.

The aqueous KF waste stream is treated to remove impurities  
30 and subjected to electrodialytic splitting as described above. The resulting product streams may be further treated to concentrate and purify the streams. For instance, the dilute HF product stream can be concentrated to form about 35 wt % to about 38 wt % HF with known distillation technology. A 38% azeotropic concentration of HF  
35 is preferred.

The dilute HF product stream may contain low amounts of non-volatile impurities such as KF, sulfates, phosphates, sodium

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fluoride, and heavy metals. For instance, 1-2% KF may result from transport of KF across the membranes. These impurities are undesirable in the 38% HF product and, therefore, must be removed before distilling.

5 Any method to remove these impurities may be used such as flash evaporation of the 10% HF stream whereby non-volatiles are removed through the bottoms and HF and water are removed overhead. Some HF and water remain in the bottoms. The flash bottoms can be recycled to the pH adjustment step prior to carbon  
10 treatment. This recycle not only recovers the fluoride and potassium values that would otherwise be lost but also avoids disposal costs. Recycle of the flash bottoms also recycles any heavy metals and results in increasing the concentration of these impurities. At some high concentration of these impurities, membrane fouling may occur;  
15 therefore, a purge stream may be taken off the recycle loop to prevent fouling of the membrane.

The overhead stream from the flash evaporation contains about 10% HF. This stream is subjected to a second distillation resulting in a water overhead stream and, preferably, a pure 38% HF  
20 bottoms stream. The water from the overheads can be recycled to the cell stack for use as makeup water, which avoids the necessity of a water treatment facility. The 38% HF from this distillation can be used, as is, by a customer, such as for stainless steel pickling. The 38% HF could also be converted to anhydrous HF by known  
25 technology or fortified to any higher strength by the addition of anhydrous HF.

The dilute KOH product stream recovered from the water splitting cell may contain up to about 3% KF from transport of KF across the membranes or from the use of electrodialytically depleted  
30 KF as makeup H<sub>2</sub>O to the base loop. KOH can be transported back to the source to be used for scrubbing more HF streams to produce more KF. The dilute KOH stream can also be concentrated to 45%, a commodity chemical. The small amount of KF in the KOH does not affect the KF recovery as the KF is not lost from the system.

35 Figure 3 is a flow diagram which represents one embodiment of the present invention. As discussed, not all the steps may be necessary to treat the KF waste stream. The aqueous KF waste

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stream (40) is obtained from one or more sources. Any insoluble organics or inorganics are removed (70) and then the waste stream (42) is gas stripped (72). The H<sub>2</sub>O and organics effluent stream is removed and discharged and the gas stripped KF stream (44) is removed and subjected to pH adjustment (74), if necessary. The pH adjusted stream (46) is subjected to carbon adsorption (76) to remove any residual organics. The treated KF waste stream (48) is then subjected to electrodialytic water splitting to convert KF and water to HF and KOH. The dilute KOH stream (50) can be used as is or concentrated. The dilute HF stream (52) can be subjected to flash evaporation (80) if necessary and the purified dilute HF stream (54) can be concentrated by product distillation (82) to form concentrated HF (56). Residual water (60) is recycled to the water splitting cell. Residual HF and KF (58) from the flash distillation is returned to the pH adjustment step, or recycled to the salt loop of the water splitter.

#### Examples

Analysis of the streams in the foregoing examples was completed by common analytical techniques such as: acid/base titration, Atomic Adsorption Spectrophotometry, and Fluoride Specific Ion Electrode. Electrical measurements were with a digital volt/ohm meter.

A 15x20 centimeter hexagonal cell stack consisting of four cells was used in Examples 5-10 and 15 through 18. Each cell unit consisted of a bipolar, anion and cation membranes arranged as shown in Figure 2 to form acid, salt and base compartments. The active surface area of each membrane was 23 cm<sup>2</sup>. In all of the Examples direct current was passed through the cell stack using a nickel anode and a stainless steel cathode. The base product formed is maintained at about 18% KOH, the acid product is maintained at about 10% HF. The depleted salt stream is recycled and used in place of dilution water.

#### Examples 1 to 4

Steam stripping in a pilot plant operation was conducted for removal of the bulk organics from ASO-KF-2, with 3700 ppm TOC. Steam stripping was done in an apparatus shown in Figure 1.

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ASO-KF-2 was preheated to 95-105°C and pumped to the top of the column. Low pressure steam (~5 psig) was introduced at the bottom of the column with and without superheat. The stripped ASO-KF-2 was collected in the bottom reservoir. Vapors exiting the column top with steam and organics were condensed and collected. The results are given in Table 1. The results indicate that the bulk of the organics are removed from ASO-KF.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Start % KF	14.8	14.8	17.8	17.8
Start non-acetic ppm TOC	3100	3100	3100	3410
End % KF	16.4	13.4	23.8	23.8
End ppm non-acetic TOC	1100	800	1500	1600
End ppm non-acetic TOC at start % KF	920	960	940	1020
% non-acetic TOC removal	70	70	70	70

The above results demonstrate that 70% of the non-acetate organics can be removed from ASO-KF-2 by steam stripping. The % KF in the stripped material may be higher or lower depending on the stripping conditions. Optimization of the stripping conditions may lead to greater organics removal.

Most of the organics are removed in a single pass. This means that KF need only be run through the stripper once, and no recycle is necessary, indicating that a commercial process is viable. The actual amount removed will be determined by the organic species present and the steam stripping conditions used in a commercial process.

Based on the above results, steam stripping can be used for removal of the bulk of the volatile organics from other ASO-KF sources. Refinery to refinery variability of the ASO-KF feeds should not have a significant effect on the removal of the bulk of organics by steam stripping.

#### Examples 5-8

These examples demonstrate the use of ARN-KF (low impurity feed) from two different refineries. The streams were analyzed, pH adjusted and passed through the four cell water splitting stack with

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and without carbon treatment. The results of the analysis of the untreated materials are given in Table 2.

Table 2

	ARN-KF-1	ARN-KF-2
% KF	12.3	27.5
% KOH	1.8	-
% HF	-	0.5
ppm Si	18	8
ppm Al	68	-
ppm TOC	19	17
Color	clear	yellow

5

ARN-KF-1 was adjusted to pH 6-7 with aqueous HF. Carbon dioxide was released from the decomposition of carbonates. A precipitate that formed was identified as potassium sodium aluminum fluoride and potassium hexafluorosilicate ( $K_2NaAlF_6 + K_2SiF_6$ ). The solution was then filtered to remove the solids. Thus the pH adjustment removed harmful impurities in the KF feed.

10

**Example 5**

The pH adjusted and filtered ARN-KF-1 was passed through a carbon bed. The material exiting the carbon bed had 4 ppm TOC. This material was fed to the water splitting cell described above. The results are shown in the Table 4 below. The data indicate successful operation of the cell.

15

**Example 6**

The pH adjusted and filtered ARN-KF-1 from above was passed through the water splitting cell stack without carbon treatment. The results are shown in Table 3 below. The slight increase in the volts/cell indicates a potential problem in a long term run.

20

Table 3

	Example 5 ARN-KF-1	Example 6 ARN-KF-1
Carbon treat	yes	no
Hrs. operated	220	188

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% HF	~10	~10
% KOH	~18	~18
Volts/cell	2.4-2.5	2.6-2.7
Fouling	no	not significant

**Example 7**

ARN-KF-2 was diluted to about 20% with deionized water and passed through the carbon bed without pH adjustment (pH ~6). The exit TOC was 11.4 ppm. The material was successfully passed through the water splitting cell. The results are shown in Table 4.

**Example 8**

The diluted ARN-KF-2 without carbon treatment was passed through the water splitting cell. The results are shown in Table 4. Again, the slight increase in the volts/cell indicates a potential problem in a long term run.

**Table 4**

	Example 7 ARN-KF-2	Example 8 ARN-KF-2
Carbon treat	yes	no
Hrs. operated	792	557
% HF	~10	~10
% KOH	~18	~18
Volts/cell	2.5-2.6	2.7-2.8
Fouling	no	not significant

The above examples demonstrate that ARN-KF can be processed to produce good quality HF and KOH products without fouling the membrane. The results indicate that carbon treatment is not required when the metal and organic impurities are very low. However, to remove color bodies and to ensure smooth successful long term operation of the cell stack, carbon treatment is preferred. These examples also demonstrate that KF from different refineries can be processed. Refinery to refinery variability does not affect the process of this invention.

**Examples 9-13**

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These examples demonstrate the use of ASO-KF from two different refineries. They were analyzed, pH adjusted as necessary, and passed through the water splitting cell with and without carbon treatment. Results of the analysis of the untreated samples are shown in Table 5.

Table 5

	ASO-KF-1	ASO-KF-2
% KF	20.0	18.0
% KOH	-	-
% HF	1.0	0.2
ppm Si	Tr	Tr
ppm Al	Tr	Tr
ppm TOC	8000	3700
Color	clear	yellow

**Example 9**

ASO-KF-1 was acidic and therefore, no carbonates were present. The pH was adjusted to pH 6-7 by adding KOH. No metal precipitates or carbon dioxide were observed.

The ASO-KF-1 was then passed through a carbon bed. The first 5 gallons of material had 3 ppm TOC. The next 9 gallons of material through the bed showed 6850 ppm TOC. This indicated breakthrough of organics through the carbon bed.

The first 5 gallons of material through the carbon bed were then passed through the water splitting cell stack described above. The results are shown in Table 6. This completely carbon treated material was successfully processed.



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**Example 10**

The next 9 gallons of partially treated ASO-KF-1 (6850 ppm TOC) was passed through the cell stack described above. The results are shown in Table 6. Cell stack operation was stopped after about 16 hours. Both anion and cation membrane resistance had increased three fold indicating severe fouling.

**Table 6**

	Example 9 ASO-KF-1	Example 10 ASO-KF-1
Carbon treat	yes	partial
Hrs. operated	160	16
% HF	~10	~10
% KOH	~18	~18
Volts/cell	2.2	2.2-> 4
Fouling	no	rapid

10

**Example 11**

ASO-KF-2 had a pH of 6.5 and no pH adjustment was required. After carbon treatment, the material had 1200 ppm TOC. The carbon treated material was passed through the cell stack described above. The results are shown in Table 7. Operation was successful.

15

**Example 12**

The ASO-KF-2 was not carbon treated before entering the cell stack. The cell voltage increased from 2.2 to 3.4 volts almost immediately indicating fouling of the membranes. The results are given in Table 7.

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Table 7

	Example 11 ASO-KF-2	Example 12 ASO-KF-2
Carbon treat	yes	no
Hrs. operated	800	12
% HF	~10	~10
% KOH	~18	~18
Cation resistance	2.2	2.2 -> 3.4
Fouling	no	rapid

Examples 13 and 14

5 To further confirm the effects of organics on membrane fouling, static soak tests were also conducted in the two non-carbon treated ASO-KF solutions described above. The results are shown in Table 8. The results indicate that non-carbon treated ASO-KF will seriously foul the membranes.

10

Table 8

	Example 13 ASO-KF-1	Example 14 ASO-KF-2
Days in soak	38	22
Bipolar selectivity	$0.94 \geq 0.87$	not measured
Cation selectivity	$0.75 \geq 0.53$	not measured
Cation resistance	$2.6 \geq 20 \text{ Ohm cm}^2$	$2.8 \geq 14.5 \text{ Ohm cm}^2$

15 The above results indicate that noncarbon treated ARN-KF may cause problems in a long term run. Carbon treated KF streams, on the other hand, operate successfully in the cell stack to produce a quality product.

20 ASO-KF-2 carbon treatment reduced the organics from 3700 ppm TOC to 1200 ppm TOC. Although the TOC was high, cell stack operation was successful. Carbon treatment had removed the harmful impurities.

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**Examples 15 and 16**

The following examples demonstrate that commercially available carbon from different manufacturers do not affect the harmful impurities removal from ASO-KF.

- 5        The ASO-KF-2 described above was treated with different carbons (Calgon PCB and Norit Carbon from North America Carbon Co.) and passed through the cell stack described above. The results are shown in Table 9. The ASO-KF was successfully processed in the cell stack.

10

**Table 9**

	Example 15 Carbon-A	Example 16 Carbon-B
Before TOC, ppm	3700	3700
After TOC, ppm	565	560
Cell run, hours	168	100
Volts/cell	2.2	2.2
% HF	~10	~10
% KOH	~18	~18
Foul	no	no

The above results indicate that any commercially available activated carbon can be used for removal of the harmful impurities that can foul the membrane.

15

**Examples 17-18**

These examples illustrate the effects of steam stripped ASO-KF-2 with and without carbon treatment on the cell stack. The results are shown in Table 10.

**Table 10**

	Example 17	Example 18
Carbon treat	yes	no
ppm TOC in	1800	1800
ppm TOC out	550	1800
Cell stack hours	226	69
Volts/cell	steady 2.2	increase to 3.4
% HF	~10	~10
% KOH	~18	~18

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The above results demonstrate that steam stripping does not remove all the organics harmful to the membranes. Carbon treatment is required to remove the remaining harmful impurities.

5 Since steam stripping can remove the major portion of the organics economically, the process of this invention employs steam stripping to remove > 50% of the organics and a carbon bed as the polishing step to remove the remaining harmful impurities for successful membrane operation.

#### 10 Example 19

This example demonstrates lab scale conversion ~10% HF from the processing of ASO-KF-2 in cell the stack to 35-38% HF final product using known distillation technology. The ~10% HF from the cell stack contained undesirable impurities such as KF, sulfates, 15 phosphates, and trace heavy metals. These non-volatiles were separated by a single stage flash distillation step where the HF and water were taken overhead. The non-volatiles remained in the bottoms.

20 The overheads from the flash distillation were subjected to a second distillation to remove the water and concentrate the HF up to the azeotrope concentration of 38%. The actual lab product made contained 35.4% HF. More separating plates in the laboratory column would increase the % HF to 38%.

25 The product was analyzed and the results indicate excellent quality consistent with a 70% HF that is an article of commerce.

Table 11

	Example 19	70 % Specs.
ppm TOC	3	none
ppm NVA	12	50
ppm SO <sub>2</sub>	< 5	< 50
ppm As	0.2	< 10
ppm Cl	43	none
ppm H <sub>2</sub> SiF <sub>6</sub>	7	100

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The lab product described above was tested by the stainless steel pickling industry and found to be an acceptable substitute for the 70% HF.

5 The 38% HF made in the process of this invention can be converted to anhydrous HF by known technology.

10 The KOH product obtained in the operation of the cell stack described above was analyzed and found to contain 1-2% KF from diffusion in the cell stack and some organics not removed in the pretreatment step. This product is suitable for scrubbing acidic fluoride waste streams with no further treatment. The 18% KOH can be converted to 45% KOH for other market uses with known technology.

-20-

WHAT IS CLAIMED IS:

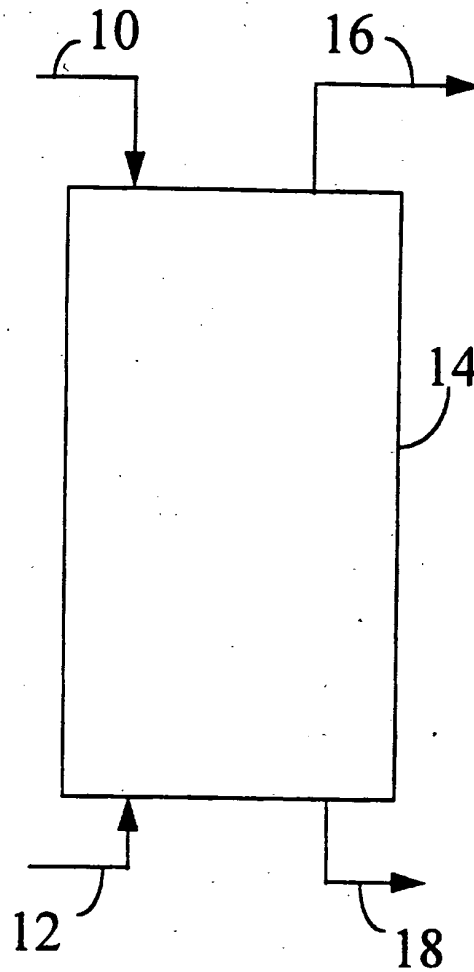
1. A process for treating an aqueous KF waste stream comprising at least one treatment step selected from the group consisting of inert gas stripping the aqueous KF waste stream, 5 passing said waste stream through a carbon bed, concentrating said waste stream or a combination thereof to remove dissolved organic compounds.
2. The process as recited in claim 1 wherein the inert gas stripping is conducted with a gas selected from steam, air, N<sub>2</sub>, 10 helium, methane or burner discharge waste gas.
3. The process as recited in claim 1 wherein at least 50 to 85% of the undesirable organics is removed.
4. The process as recited in claim 1 wherein the stripping temperature is at least about 100°C.
- 15 5. The process as recited in claim 1 further comprising splitting the KF in the treated KF waste stream by introducing the treated KF waste stream into an electrodialytic water splitting apparatus having at least one water splitting cell, under the influence of direct current.
- 20 6. The process as recited in claim 5 wherein the treated KF waste stream introduced into the water splitting cell contains about 15 to about 20 wt % KF.
7. The process as recited in claim 1 further comprising removing insoluble organic or inorganic materials from the aqueous 25 KF waste stream prior to the treatment step of claim 1.
8. The process as recited in claim 1 further comprising adjusting the pH of the treated KF waste stream to about 6 to about 8 to decompose carbonates and to precipitate silica and heavy metal compounds.

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9. The process as recited in claim 1 wherein the aqueous KF waste stream is an alkylation KF waste stream.
10. The process of claim 1 wherein said treatment step is concentrating said waste stream to a KF concentration which is at least about 20 weight % such that about 50 to about 95% of said dissolved organic compounds are removed.
- 5

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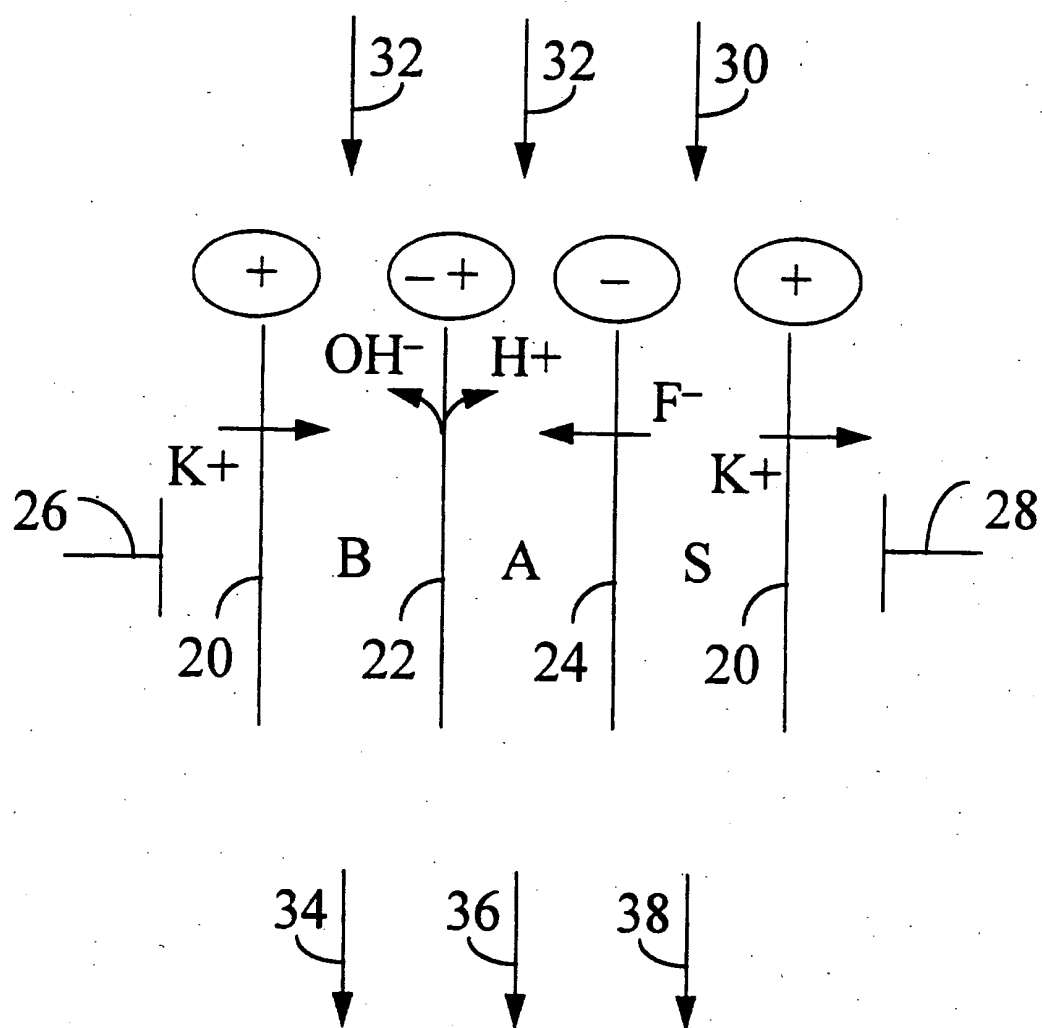
Fig. 1





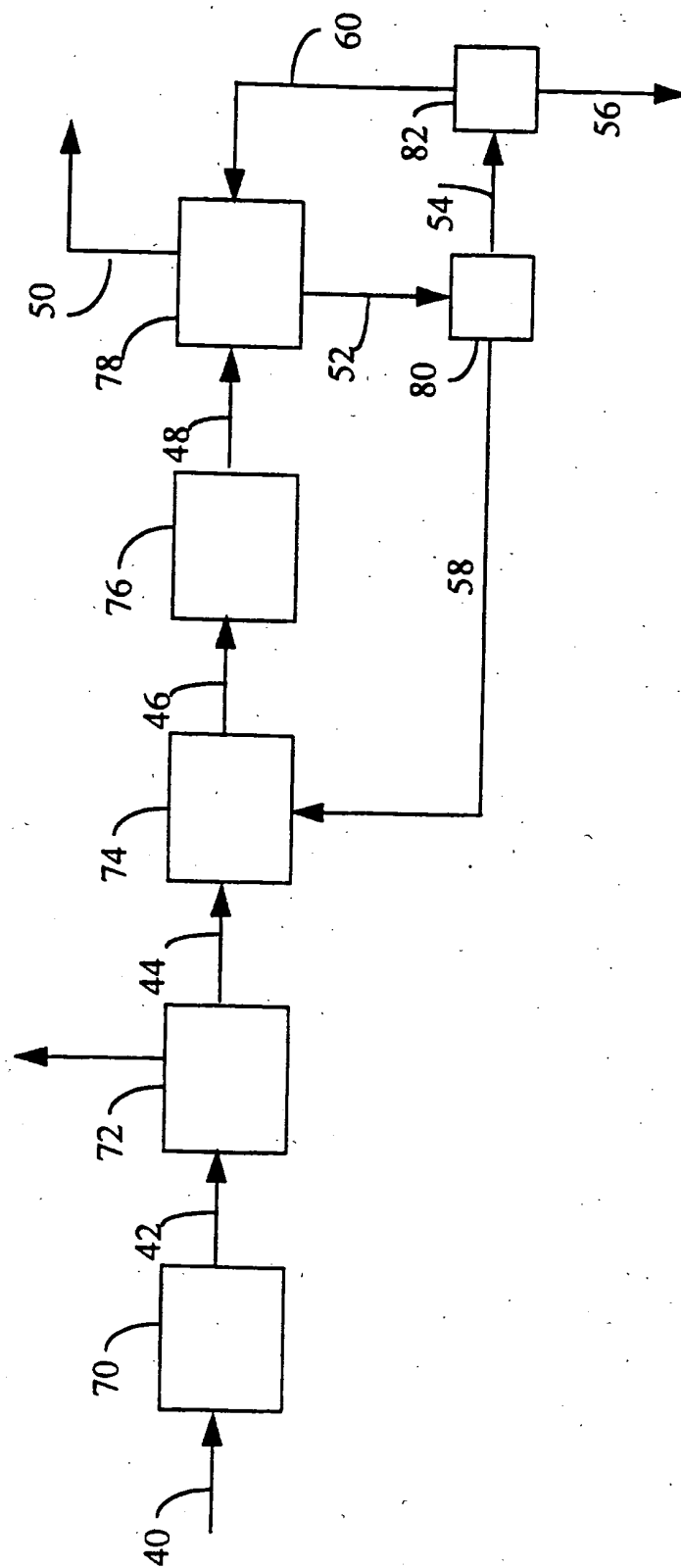
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Fig. 2



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Fig. 3



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## (57) Abstract

The present invention is directed to a process for treating an aqueous KF waste stream comprising at least one treatment step selected from the group consisting of inert gas stripping the aqueous KF waste stream, passing said waste stream through a carbon bed, concentrating said waste stream or a combination thereof to remove dissolved organic compounds. The present invention is also directed to subjecting the treated KF waste stream to electrodialytic splitting in a water splitting cell to form HF and either KOH or an acid depleted salt stream. The dilute HF can be concentrated to a concentrated and commercially viable product.

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/11584

A. CLASSIFICATION OF SUBJECT MATTER  
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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 111, no. 24, 11 December 1989 Columbus, Ohio, US; abstract no. 218891, XP002001119 see abstract & JP,A,01 130 783 (SHINKO PFAUDLER CO., LTD.) 23 May 1989	1,3,5-10
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 148 (C-0928), 13 April 1992 & JP,A,04 006104 (NIPPON LIGHT METAL CO LTD), 10 January 1992, see abstract	1
A	US,A,4 713 231 (CAMPBELL KENT D ET AL) 15 December 1987 see column 2, line 3 - line 26	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 976 946 (I. R. KING) 11 December 1990 see column 1, line 37 - column 2, line 41 see column 2, line 59 - column 3, line 8 see column 3, line 52 - line 61 see claims ---	1
A	CHEMICAL ABSTRACTS, vol. 87, no. 20, 14 November 1977 Columbus, Ohio, US; abstract no. 154227n, XP002001120 see abstract & OTKRYTIYA, IZOBRET., PROM. OBRAZTSY, TOVARNYE ZNAKI, vol. 54, no. 30, 1977, USSR, page 47 ---	1
A	US,A,3 787 304 (F. P. CHLANDA ET AL.) 22 January 1974 cited in the application see column 1, line 48 - column 2, line 14 see column 2, line 47 - column 3, line 50 see column 4, line 34 - line 44 see claims; example 1 -----	1,5

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 95/ 11584

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
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This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims : 1 (partially), 3, 5-10 (partially)
2. Claims : 1 (partially), 2-10 (partially)
3. Claims : 1 (partially), 3, 5-10 (partially)

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3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
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- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A-3787304	22-01-74	CA-A- 995174 DE-A- 2303072 FR-A,B 2169951 GB-A- 1413742 JP-C- 1108617 JP-A- 48088095 JP-B- 56049842	17-08-76 16-08-73 14-09-73 12-11-75 13-08-82 19-11-73 25-11-81